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## Electronic Supplementary Information for

# Applying intermolecular hydrogen bonding to exploit TADF emitters for high-performance orange-red non-doped OLEDs

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#### **Experimental Section**

**General information:** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 600 spectrometer at room temperature. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe. Single-crystal X-ray structure analysis was obtained using Bruker D8 Venture X-ray single crystal diffractometer. UV-vis absorption spectra were recorded on a Hitachi U-3900 spectrophotometer. PL spectra and phosphorescent spectra were recorded on a Hitachi U-3900 spectrophotometer. PL spectra and phosphorescent spectra were recorded on a Hitachi U-3900 spectrophotometer. PL spectra and phosphorescent spectra were recorded on a Hitachi U-3900 spectrophotometer. Transient fluorescence decays and fluorescence quantum yield were measured with an Edinburgh Instruments FLS980 spectrometer. Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature. Deaerated DMF was used as solvent with tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) (0.1 M) as the supporting electrolyte. The cyclic voltammograms (CV) were obtained at scan rate of 0.05 V·S<sup>-1</sup> with platinum electrode as the working/counter electrode and an Ag/AgCl electrode as the reference electrode with standardized against ferrocene/ferrocenium. The density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using B3LYP/6-31g(d) basis set using Gaussian 09. The spin-density distributions (SSDs) of the lowest excited triplet states were analyzed using a multifunctional wavefunction analyzer (Multiwfn 3.7)<sup>1</sup> and and visualized with VMD program (1.9.3).

**Fabrication and measurement of OLED devices:** The OLEDs were fabricated on the indium-tin oxide (ITO) coated transparent glass substrates, the ITO conductive layer has a thickness of ca. 100 nm and a sheet resistance of ca. 30  $\Omega$  per square. The substrates waswere cleaned with ethanol, acetone and deionized water, and then dried in an oven, finally exposed to UV ozone for 15 min. All of the organic materials and metal layers were thermal evaporated under a vacuum of ca. 10<sup>-5</sup> Torr. Four identical OLED devices were formed on each of the substrates and the emission area of 0.1 cm<sup>2</sup> for each device. The EL performances of the devices were measured with a PHOTO RESEARCH Spectra Scan PR 655 PHOTOMETER and a KEITHLEY 2400 Source Meter constant current source at room temperature.



Scheme S1. Synthetic procedure of Pyrimidine-based TADF emitters.

Synthesis of 4-(4-bromophenyl)-2,6-di(pyridin-3-yl)pyrimidine (Intermediate b): To a solution of 4-

bromobenzaldehyde (0.92 g, 5.0 mmol) and 3-acetylpyridine ( $606 \,\mu$ L, 5.5 mmol) in 50 mL MeOH, 1.75 mL aqueous 1M NaOH was added dropwise and stirred for 5 min. During the addition of NaOH, a precipitate was formed which was filtered off. Drying in vacuo yielded 1.20 g (83.3%) of intermediate **a** as a white solid and used without further purification.

Then to a solution of pyridine-5-carboximidamide hydrochloride (0.72 g, 4.6 mmol) and intermediate  $\mathbf{a}$  (1.44 g, 5.0 mmol) in EtOH (50 mL) in a 100 mL flask, KOH (0.77 g, 13.6 mmol) of 5ml aqueous was added and the mixture was refluxed for 12h. After the completion of the reaction and cooled to ambient temperature, the white precipitate was collected by filtration, and washed with water. After dried *in vacuo* for 24 h, white fluffy solid (Intermediate  $\mathbf{b}$ , 0.60 g, 33.9%) was obtained and used without further purification.

*Synthesis of 6-(4-bromophenyl)-2-(pyridin-3-yl)-4,5'-bipyrimidine (Intermediate d):* To a solution of 4-bromobenzaldehyde (0.92 g, 5.0 mmol) and 5-acetylpyrimidine (0.67 g, 5.5 mmol) in 50 mL MeOH, 5.30 mL aqueous 10% Na<sub>2</sub>CO<sub>3</sub> was added dropwise and stirred for 2 hours. During the addition of Na<sub>2</sub>CO<sub>3</sub>, a precipitate was formed which was filtered off. Drying in vacuo yielded 1.30 g (89.7 %) of intermediate **c** as a light-yellow solid and used without further purification.

Pyridine-5-carboximidamide hydrochloride (0.47 g, 3.0 mmol), intermediate c (0.87 g, 3.0 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 g, 6.0 mmol) were added to a 100 mL flask. 30 ml DMSO was added and the mixture was refluxed for 12h. After the completion of the reaction and cooled to ambient temperature, the white precipitate was collected by filtration, and washed with water. The residue was purified by column chromatography on silica gel (eluent: EtOAc/THF=10/1) to afford white fluffy solid (Intermediate d, 0.30 g, 25.6%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  9.86 (s, 1H), 9.56 (s, 2H), 9.40 (s, 1H), 8.90 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.78 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 2H), 8.04 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.49 (dd, *J* = 8.0, 4.8 Hz, 1H).

Synthesis of 10-(4-(2,6-di(pyridin-3-yl)pyrimidin-4-yl)phenyl)-10H-phenoxazine (PyPmP): Phenoxazine (0.38 g, 2.1 mmol), Intermediate **b** (0.78 g, 2.0 mmol), palladium(II) acetate (13.5 mg, 0.06 mmol), sodium tert-butoxide (0.58 g, 6.00mmol) in a 100-mL two-necked flask, with stirring under argon atmosphere, was added tri-tert-butylphosphine (10% in Toluene, 0.47 mL) and toluene (50 mL). The mixture was stirring at 90 °C for 12h. The cooled mixture was partitioned between EtOAc and water. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO4 and concentrated by rotary evaporator. The residue was purified by column chromatography on silica gel (eluent: EtOAc/THF=10/1) to afford PyPmP (0.55 g, 56.1%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  9.93 (d, *J* = 1.9 Hz, 1H), 9.48 (d, *J* = 2.2 Hz, 1H), 9.06 (d, *J* = 7.9 Hz, 1H), 8.81 (ddd, *J* = 15.6, 4.8, 1.7 Hz, 2H), 8.64 (dt, *J* = 8.2, 1.9 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 2H), 8.16 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.56 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.73 (dd, *J* = 7.9, 1.5 Hz, 2H), 6.68 (td, *J* = 7.6, 1.5 Hz, 2H), 6.62 (td, *J* = 7.7, 1.6 Hz, 2H), 6.03 (dd, *J* = 8.0, 1.5 Hz, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  164.57, 163.62, 163.09, 162.72, 158.60, 151.91, 148.86, 148.46, 143.98, 142.14, 136.98, 136.56, 134.91, 133.88, 133.71, 132.51, 131.64, 130.08, 123.94, 123.27, 121.72, 115.66, 113.27, 111.24. MS (EI). Calcd for C<sub>32</sub>H<sub>21</sub>N<sub>5</sub>O ([M]<sup>+</sup>): m/z 491.55. Found: m/z 491.58.

*Synthesis of 10-(4-(2-(pyridin-3-yl)-[4,5'-bipyrimidin]-6-yl)phenyl)-10H-phenoxazine (PmPmP):* PmPmP was synthesized by the same procedure using intermediate **d** instead of intermediate **b**. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  9.90 (dd, J = 2.2, 0.9 Hz, 1H), 9.60 (s, 2H), 9.42 (s, 1H), 8.94 (dt, J = 8.0, 1.9 Hz, 1H), 8.80 (d, J = 4.8 Hz, 1H), 8.52 (d, J = 8.4 Hz, 2H), 8.13 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.51 (ddd, J = 8.0, 4.8, 0.9 Hz, 1H), 6.73 (dd, J = 7.9, 1.6 Hz, 2H), 6.69 (td, J = 7.6, 1.4 Hz, 2H), 6.62 (ddd, J = 8.0, 7.3, 1.6 Hz, 2H), 6.03 (dd, J = 8.0, 1.4 Hz, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  164.84, 163.67, 160.53, 160.30, 155.60, 151.96, 150.21, 143.98, 142.33, 136.34, 135.76, 133.84, 132.67, 131.69, 130.44, 130.10, 123.48, 123.27, 121.76, 115.69, 113.26, 110.84. MS (EI). Calcd for C<sub>31</sub>H<sub>20</sub>N<sub>6</sub>O ([M]<sup>+</sup>): m/z 492.54. Found: m/z 492.23.

The crystal structure data of PyPmP and PmPmP have been deposited in Cambridge Structural Database as CCDC 2093258 and 2093260 respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### **Thermal properties**



Figure S1. TGA and DSC of PyPmP (a and c) and PmPmP (b and d).

#### **Theoretical simulations**



**Figure S2.** Calculated adiabatic excited states energies and NTO analysis of PyPmP and PmPmP (red for the hole and blue for the particle). The isovalue is 0.02.

#### **Photophysical properties**



**Figure S3.** Normalized fluorescence spectra of (a) PyPmP and (b) PmPmP amorphous neat film at room temperature, and corresponding normalized fluorescence and phosphorescence spectra at 77K ((c) PyPmP and (d) PmPmP).



**Figure S4.** Transient PL decay curves of (a) PyPmP and (b) PmPmP non-doped films in time range of 5.7 µs at various temperatures excited at 373 nm; and normalized time-resolved prompt (PF) and delayed (DF) fluorescent spectra of (c) PyPmP and (d) PmPmP non-doped films at 300 K.



**Figure S5.** Transient PL decay curves for delayed emission of PyPmP and PmPmP 10 wt% and 100 wt% (non-doped) in CBP films in a time range of 53 ns (a and c) and 5.7 µs (b and d) at 300 K excited at 373 nm.

#### **Carrier mobility**



**Figure S6.** Hole- and electron-only current density-voltage characteristic of the amorphous neat films of PyPmP (Black) and PmPmP (Red). Hole-only devices: ITO/MoO3 (12 nm)/TADF emitters (30 nm)/MoO3 (12 nm)/Al (100 nm). Electron-only devices: ITO/Al (40 nm)/LiF (1 nm)/ TADF emitters (30 nm)/LiF (1 nm)/Al (100 nm).

#### **Molecular orientation**



**Figure S7.** Results of VASE measurements; extinction coefficient k (black) and refractive index n (red). The solid and dashed lines represent spectra for the ordinary and extraordinary optical constants ((a) PyPmP and (b) PmPmP).

### **Crystal results**



Figure S8. Molecular packing modes of (a) PyPmP and (b) PmPmP in the single crystals.

#### **EL performance**



Figure S9. The structures configuration of the OLEDs and the molecular structures.



**Figure S10.** Normalized EL spectra and the PE-luminance-EQE characteristics of PyPmP (a and b) and PmPmP (c and d) with various doping ratios. Purple, indigo, blue, green, yellow, and orange for 5 wt%, 10 wt%, 20 wt%, 30 wt%, 70 wt%, and 100 wt% respectively.

Table S1. Structure information of PyPmP and PmPmP at optimal ground state.

|       | θ1 (°) | $\theta_2(^{\circ})$ | θ <sub>3</sub> (°) |
|-------|--------|----------------------|--------------------|
| PyPmP | 85.4   | 22.3                 | 6.0                |
| PmPmP | 83.3   | 22.0                 | 5.8                |

Table S2. Summary of key physical properties of PyPmP and PmPmP.

|       | λ <sub>abs</sub> <sup>a</sup><br>(nm) | λ <sub>PL</sub> b<br>(nm) | $\Phi_{\mathrm{F}}^{\mathrm{c}}$ (%) | $S_1/T_1/\varDelta E_{ST}^{d}$ (eV) | $	au_{\rm p}/	au_{\rm d}^{\rm e}$ (ns/\mu s) | HOMO/LUMO <sup>f</sup><br>(eV) |
|-------|---------------------------------------|---------------------------|--------------------------------------|-------------------------------------|--|--------------------------------|
| PyPmP | 316/415                               | 542                       | 65.9                                 | 2.49/2.45/0.04                      | 20.4 (15.7)/ 0.7 (1.1)                       | -5.30/-3.06                    |
| PmPmP | 317/422                               | 563                       | 42.9                                 | 2.40/2.35/0.05                      | 20.9 (17.4)/0.5 (0.9)                        | -5.36/-3.19                    |

Determined from <sup>a</sup>UV–vis absorption spectra and <sup>b</sup>fluorescent spectra measured in toluene solution. <sup>c</sup>Absolute PL quantum yield evaluated using an integrating sphere of PyPmP and PmPmP amorphous neat films. <sup>d</sup>Determined by the onset of fluorescence/phosphorescence spectrum of the neat film measured in 77K,  $\Delta E_{ST}$  calculated as  $\Delta E_{ST} = S_1 - T_1$ . <sup>c</sup>The prompt and delayed component in transient PL of PyPmP and PmPmP amorphous neat films under vacuum condition. Results of the 10 wt% doped in CBP films are listed in parentheses. <sup>f</sup>HOMO was determined from the onset of oxidation potential with respect to ferrocence; LUMO was determined from the onset of reduction potential with respect to ferrocene.

|           | Emitters   | Peak<br>(nm) | Max CE/ PE/ EQ |                                    |   |              |
|-----------|------------|--------------|----------------|------------------------------------|---|--------------|
| Ref       |            |              | Maximum        | $@ 10^3 \text{ cd } \text{m}^{-2}$ | EQE <sub>Roll-off</sub> <sup>a</sup><br>(%) | CIE (x, y)   |
| This work | PyPmP      | 576          | 50.5/53.5/18.8 | 45.1/33.3/16.7                     | 11.2  | (0.50,0.49)  |
|           | PmPmP      | 596          | 23.3/22.1/11.3 | 20.4/14.6/10.0                     | 11.5  | (0.56,0.44)  |
| [2]       | PTZ-BP     | 577          | -/-/7.6        | -/-/~6.1                           | 19.7  | -            |
| [3]       | OPDPO      | 586          | 37.6/14.8/16.7 | 26.9/10.8/11.8                     | 29.3  | -            |
|           | PCZ-CB-TRZ | 586          | 16.7/7.6/11.0  | -                                  | -   | -            |
| [4]       | 2PCZ-CB    | 590          | 19.9/11.2/9.2  | -                                  | -   | -            |
|           | TPA-CB-TRZ | 631          | 12.0/7.9/10.1  | -                                  | -   | -            |
| [5]       | SFDBQPXZ   | 584          | 24.3/22.5/10.1 | 14.2/6.3/6.0                       | 39.6  | -            |
| [5]       | DFDBQPXZ   | 588          | 21.0/20.6/9.8  | 9.8/4.2/4.7                        | 52.0  | -            |
| [6]       | PFDMPE-R05 | 606          | 10.3/3.2/5.6   | -/-/~0.8                           | 82.8  | (0.57,0.42)  |
| [7]       | SBDBQ-PXZ  | 608          | 10.5/12.0/5.6  | 9.8//5.2/5.2                       | 7.1   | (0.56,0.43)  |
|           | DBQ-3PXZ   | 616          | 7.5/6.2/5.3    | 6.2/2.9/4.4                        | 17.0  | (0.60, 0.40) |
| [8]       | TAT-DBPZ   | 626          | 7.3/7.6/5.6    | 2.9/1.5/2.2                        | 60.7  | (0.61, 0.38) |
| [9]       | Fene       | 570          | 42.2/316/14.9  | -/-/~12.8                          | 14.1  | -            |
|           | Fens       | 568          | 36.8/30.4/13.1 | -/-/~7.4                           | 43.5  | -            |
| [10]      | BEnCN-PXZ  | 592          | 10.7/4.8/4.9   | 7.2/2.2/3.2                        | 34.7  | (0.54,0.45)  |
|           | BDCN-PXZ   | 606          | 6.5/4.0/3.7    | 6.3/3.3/3.5                        | 5.4   | (0.57,0.42)  |

Table S3. Summary of the reported orange-to-red TADF emitters for non-doped OLEDs.

 $^{a}EQE_{roll-off} = (EQE_{max}-EQE_{1000})/EQE_{max}$ 

Table S4. Electroluminescence properties of the devices

|       | Doping conc. | $\lambda_{Max.}$ | CE <sub>Max</sub> / PE <sub>Max</sub> / EQE <sub>Max</sub> | CIE          |
|-------|--------------|------------------|--|--------------|
|       | (wt %)       | (nm)             | $(cd \cdot A^{-1} / lm \cdot W^{-1} / \%)$                 | (x, y)       |
| PyPmP | 5            | 532              | 71.0/65.6/21.8   | (0.33, 0.57) |
|       | 10           | 536              | 77.3/71.6/23.4   | (0.35, 0.58) |
|       | 20           | 544              | 76.7/73.8/23.0   | (0.39, 0.57) |
|       | 30           | 552              | 74.3/74.1/23.0   | (0.41, 0.56) |
|       | 70           | 564              | 57.5/58.5/19.3   | (0.47, 0.52) |
|       | 100          | 572              | 50.5/53.5/18.8   | (0.50, 0.49) |
| PmPmP | 5            | 540              | 68.5/57.0/20.6   | (0.36, 0.57) |
|       | 10           | 548              | 69.1/55.6/21.0   | (0.39, 0.56) |
|       | 20           | 560              | 65.7/59.4/20.7   | (0.43, 0.54) |
|       | 30           | 565              | 61.3/61.8/19.7   | (0.45, 0.53) |
|       | 70           | 584              | 33.5/33.4/13.8   | (0.53,0.47)  |
|       | 100          | 596              | 23.3/22.1/11.3   | (0.56, 0.44) |

#### References

- 1. T. Lu and F. Chen, J. Comput. Chem., 2012, **33**, 580-592.
- 2. N. Aizawa, C.-J. Tsou, I. S. Park and T. Yasuda, *Polym J*, 2016, 49, 197-202.
- 3. X. Chen, Z. Yang, Z. Xie, J. Zhao, Z. Yang, Y. Zhang, M. P. Aldred and Z. Chi, *Mater. Chem. Front.*, 2018, **2**, 1017-1023.
- 4. R. Furue, T. Nishimoto, I. S. Park, J. Lee and T. Yasuda, *Angew. Chem. Int. Ed.*, 2016, **55**, 7171-7175.
- L. Yu, Z. Wu, G. Xie, C. Zhong, Z. Zhu, D. Ma and C. Yang, *Chem. Commun.*, 2018, 54, 1379-1382.
- 6. Y. Yang, L. Zhao, S. Wang, J. Ding and L. Wang, *Macromolecules*, 2018, **51**, 9933-9942.

- 7. L. Yu, Z. Wu, g. xie, W. Zeng, D. Ma and C. Yang, *Chem. Sci.*, 2018, **9**, 1385-1391.
- Y. Liu, Y. Chen, H. Li, S. Wang, X. Wu, H. Tong and L. Wang, ACS Appl. Mater. Interfaces, 2020, 12, 30652-30658.
- 9. L. Zhang, Y.-F. Wang, M. Li, Q.-Y. Gao and C.-F. Chen, *Chinese Chemical Letters*, 2020, **32**, 740-744.
- Z. Qiu, W. Xie, Z. Yang, J.-H. Tan, Z. Yuan, L. Xing, S. Ji, W.-C. Chen, Y. Huo and S.-j. Su, Chem. Eng. J., 2021, 415, 128949.